

## EXTREME Na-DEPLETION IN THE PERALKALINE VOLCANIC ROCKS OF THE MIDDLE PROTEROZOIC FLOWERS RIVER CAULDRON COMPLEX, LABRADOR

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### ABSTRACT

*In ash-flow tuffs of the Flowers River cauldron complex, feldspar and, to a lesser extent amphibole, commonly exhibit replacement textures produced during a Na-depleting hydrothermal event. The most common replacement mineral is chlorite in albitic feldspar and amphibole, and sericite in K-feldspar; the degree of replacement ranges from incipient grains along fractures and cleavages to complete replacement in some feldspar porphyritic ash-flow tuffs.*

*Rocks that contain partially to completely replaced feldspar in phenocrysts or in the groundmass, usually contain little or no Na<sub>2</sub>O (< 0.1 wt. percent). Other elements, such as K, Si, and Al, and H<sub>2</sub>O also appear to be affected during the Na-depletion process. Rocks that contain high concentrations of H<sub>2</sub>O and SiO<sub>2</sub>, and low concentrations of Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O commonly contain little or no Na<sub>2</sub>O, however, the inverse is not always true.*

*Trace elements, in particular incompatible elements (e.g., Zr, Nb, U, Th, Y), show no correlation with Na-depletion or the replacement of feldspars. This observation indicates that rare-metal mineralization in the ash-flow tuffs and breccias in the upper portion of the volcanic pile is not related to the Na-depleting hydrothermal event. Preliminary data suggests that the rare-metal mineralization is probably magmatic in origin.*

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### INTRODUCTION

The Flowers River cauldron complex (FRCC) is a Middle Proterozoic (1271 Ma; Brooks *in* Hill, 1991) felsic cauldron complex consisting of a number of partially eroded nested calderas (R.R. Miller and A.M. Abdel-Rahman, unpublished data). The cauldron complex is filled with volcanic ash-flow tuffs and hypabyssal ring dykes and is floored by subvolcanic granitic rocks and rocks of the Nain Plutonic Suite. The FRCC is located near the coast of Labrador, 70 km south of Nain (Figure 1).

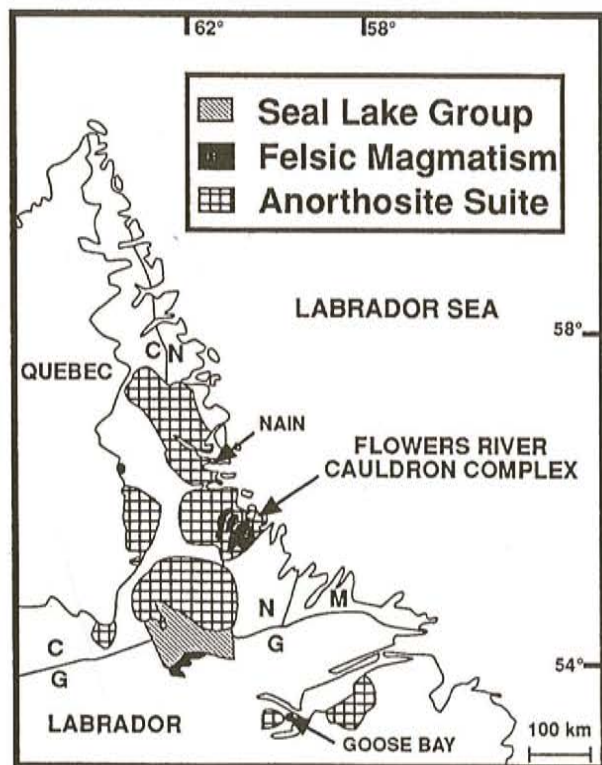
The cauldron complex consists of both volcanic and plutonic rocks belonging to the Flowers River igneous suite (Hill, 1981). The volcanic rocks of the cauldron complex are known as the Nuiklavik volcanic rocks (Beavan, 1954; Miller, 1992) and the plutonic rocks are here called the Flowers River intrusive rocks. Extensive outcrop of volcanic rocks is only known in the FRCC, whereas outcrops of the Flowers River intrusive rocks are more widespread (Hill, 1981, 1982).

Rocks of the FRCC were originally mapped in 1953 during a reconnaissance-exploration program on the coast of

Labrador (Beavan, 1954). They were further mapped in 1971, during a reconnaissance-mapping project in northern Labrador—Quebec (Taylor, 1979) and during more detailed regional mapping a few years later (Hill, 1981, 1982). The geochemistry and Rb—Sr geochronology of some of the granitic rocks of the region are given in Collerson (1982). White (1980), Hill (1981, 1982), Hill and Thomas (1983), Hill and Miller (1991) and Hill (1991) report on various other aspects of the geology, geochemistry and tectonic setting of the Flowers River igneous suite. More recent geological investigations of the FRCC have been reported in Miller (1992, 1993), Miller and Abdel-Rahman (1992) and Abdel-Rahman and Miller (1993).

Geological investigations by Hill (1981, 1982) and the follow-up geochemical work of McConnell (1984) concluded that the Nuiklavik volcanic rocks contain numerous small showings of pyrite, sphalerite, galena, molybdenite and fluorite, with high radioactivity associated with some of the pyrite-bearing rocks. White (1980), Hill (1982) and on-going geochemical investigations show that the volcanic rocks are enriched in rare metals (Y, Zr, REE), locally reaching values of economic interest (Miller 1988, 1993).





**Figure 1.** Location of the Flowers River cauldron complex; C = Churchill, G = Grenville, M = Makkovik, N = Nain.

Metasomatism in the Nuiklavik volcanic rocks has been previously discussed by White (1980), Hill (1881, 1982) and Hill and Thomas (1983). These studies documented Na loss in volcanic rocks of the FRCC. The mechanism was considered to involve alteration of feldspar phenocrysts and removal of Na from the devitrified–recrystallized groundmass. It is the aim of this report to further document the process of Na-depletion and to evaluate this metasomatic event in terms of the formation of significant concentrations of rare-metal mineralization.

## GEOLOGY

The Flowers River igneous suite intrudes Archean gneisses of the Nain Province (Hopedale block), Lower Proterozoic gneisses (reworked Archean?; Ryan, 1990; Ermanovics and Ryan, 1990) of the Churchill (Rae) Province (Hoffman, 1990), and the Proterozoic rocks of the Nain Plutonic Suite (Figure 2). In the vicinity of the FRCC, granitic and gabbroic plutons of the Nain Plutonic Suite and Nain Province gneisses are the host rocks to the Nuiklavik volcanic rocks and the granites of the Flowers River intrusive rocks.

The FRCC consists of at least seven complete, or nearly complete, partially eroded calderas and a number of caldera segments that are defined by stratigraphic discontinuities, structural data, ring dykes and slivers of cauldron floor (R.R. Miller and A.M. Abdel-Rahman, unpublished data). Individual calderas, ranging in size from 1 to 7 km in diameter, are nested to form a composite subcircular cauldron

of approximately 13 km in diameter (Figure 3). Calderas subsided a minimum of 100 to 250 m and contain minimum volumes of caldera fill from <0.5 to >5.0 km<sup>3</sup>; the estimated total fill in this cauldron complex is 30 to 50 km<sup>3</sup>. Inward-dipping beds, from 5 to 70°, characterize many of the calderas.

The preserved volcanic assemblage (Nuiklavik volcanic rocks; Figure 4) consists of (Miller, 1993): a basal unit of thinly bedded air-fall tuff and massive to faintly banded siliceous rock (Unit 1); lower amphibole-bearing porphyry (Unit 2); lower crystal-rich ash-flow tuffs (Unit 3); crystal-poor ash-flow tuffs (Unit 4); and upper ash-flow tuffs (Unit 5). Each of these volcanic units contains a number of subunits having distinctive mineralogical and textural characteristics; these include a number of porphyries with variable contents and types of phenocrysts, aphyric ash-flow tuff and lithic ash-flow tuff-breccia. Well-developed columnar joints characterize many of the sheets within these units. Many of these volcanic rocks are interpreted to represent rheo-ignimbrites.

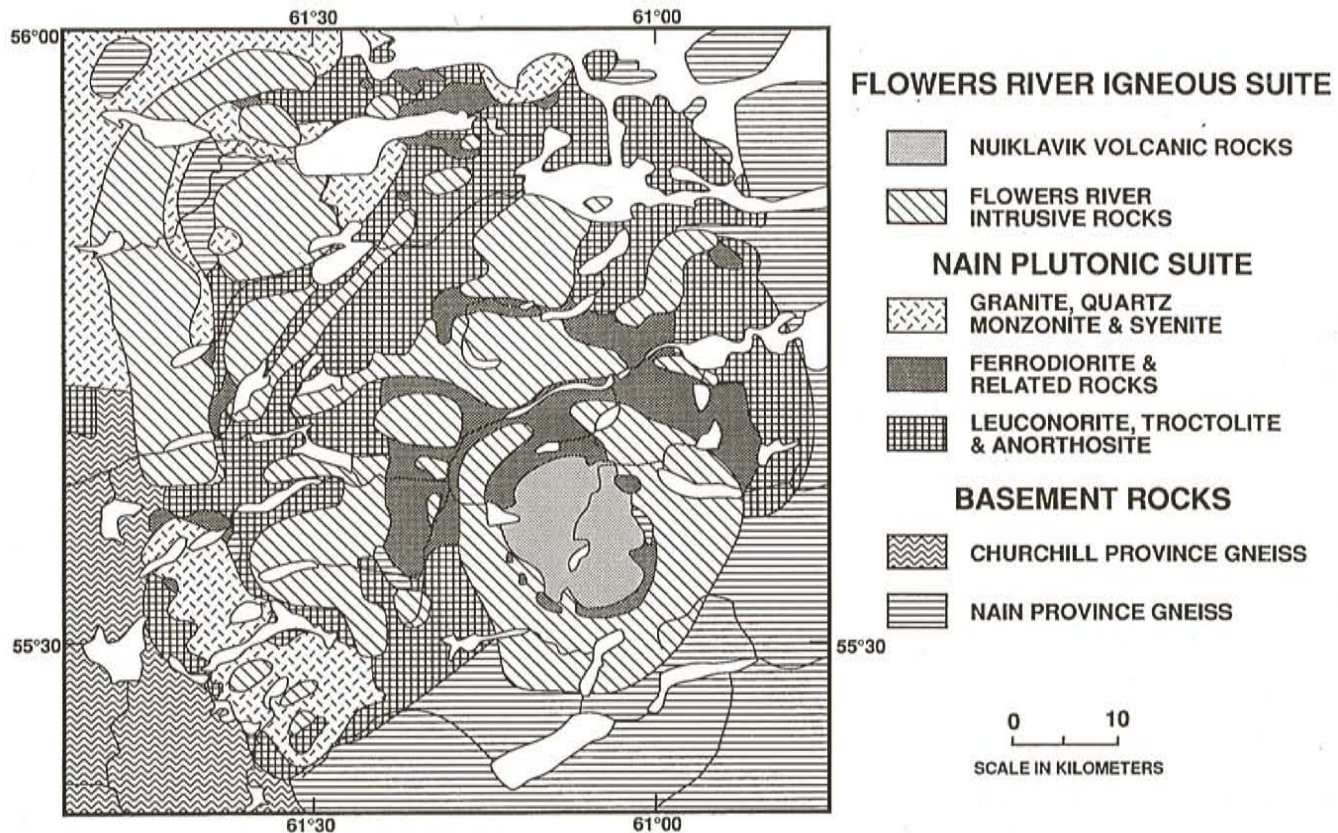
Volcanic rocks that exhibit Na-depletion are common throughout Units 2, 3 and 4 of the cauldron complex and within all recognized calderas (Figures 3 and 4). Feldspars in Unit 5, particularly in the upper units, are generally unaltered. Depletion is best displayed in feldspar-quartz ash-flow tuffs where feldspar is usually partially to completely replaced by a light-green to black mafic (chlorite-like) mineral; this is commonly characteristic of extreme Na-depletion. These rocks were field-mapped as quartz-mafic porphyries (Miller, 1992) and are most commonly found in the upper portion of the columnar-jointed porphyritic ash-flow tuffs of Unit 3. Alteration is not easily recognized in either outcrop or hand samples of aphyric and other phenocryst-poor members of the suite. The locations of samples discussed in this study can be found in Figure 5.

## PETROGRAPHY

The feldspar-quartz crystal-rich ash-flow tuff of Unit 3 displays the most obvious signs of the Na-depletion process and thus is the best unit to study with regard to textural and mineralogical changes. This unit is characterized by abundant (20 to 35 percent) subhedral feldspar phenocrysts, from 3 to 6 mm long, and subordinate (10 to 20 percent) embayed to subhedral quartz phenocrysts in a recrystallized quartz-feldspar mosaic groundmass. Broken grains and shards of quartz, and less commonly feldspar, are found in the groundmass. Feldspar phenocrysts, broken grains and groundmass feldspar are most susceptible to the alteration process.

Feldspar grains commonly exhibit alteration ranging from a dusting of sericitic alteration, to complete sericitization and from incipient alteration along cleavages to almost complete replacement by a chlorite-like mineral (Table 1); Plate 1 illustrates the progression from samples that appear relatively unaltered (Plate 1a) to samples that exhibit extreme alteration of feldspar grains (Plate 1c,d,e).





**Figure 2.** General geology in the vicinity of the Flowers River igneous suite. After Hill (1981, 1982, 1991), Thomas and Morrison (1991) and Miller (1992, 1993).

Alteration in the groundmass of the porphyritic units and in the aphyric units (e.g., the lower member of Unit 4) is not as easy to identify. Plate 1e illustrates alteration of groundmass feldspar (?) in a highly altered sample. The green mineral found in the groundmass is considered to be the same as that found replacing feldspar phenocrysts.

White (1980) reports the presence of a microcrystalline green mineral replacing albite in microperthitic feldspar and provides a partial microprobe analysis indicating enrichment of Fe and Al and depletion in Na and Si relative to unaltered albite; identification of the green mineral was not possible from the available data. Microprobe analyses indicated that Na-depletion also occurred in the groundmass. Hill (1982) reports that electron back-scatter photomicrographs of feldspar phenocrysts in volcanic porphyry indicate that Na can be almost completely absent in the groundmass even though feldspar phenocrysts appear to be relatively unaffected; similar back-scatter observations for K indicate that it is abundant in the groundmass and the feldspar phenocrysts of altered rocks.

Microscopically, the main alteration products of the microperthitic feldspars is either sericite or the chlorite-like mineral. Sericite alteration occurs on the K-feldspar phase of some microperthites and the chlorite-like mineral on the albite phase. The chlorite-like mineral ranges from weakly

to moderately pleochroic pale-brown or green to medium dark-brown or green. It commonly occurs as a microcrystalline mosaic but is also sparsely found as large grains up to 0.1 mm in some feldspars. Anomalous interference colours, the habit and pleochroism suggest that this mineral is a member of the chlorite family.

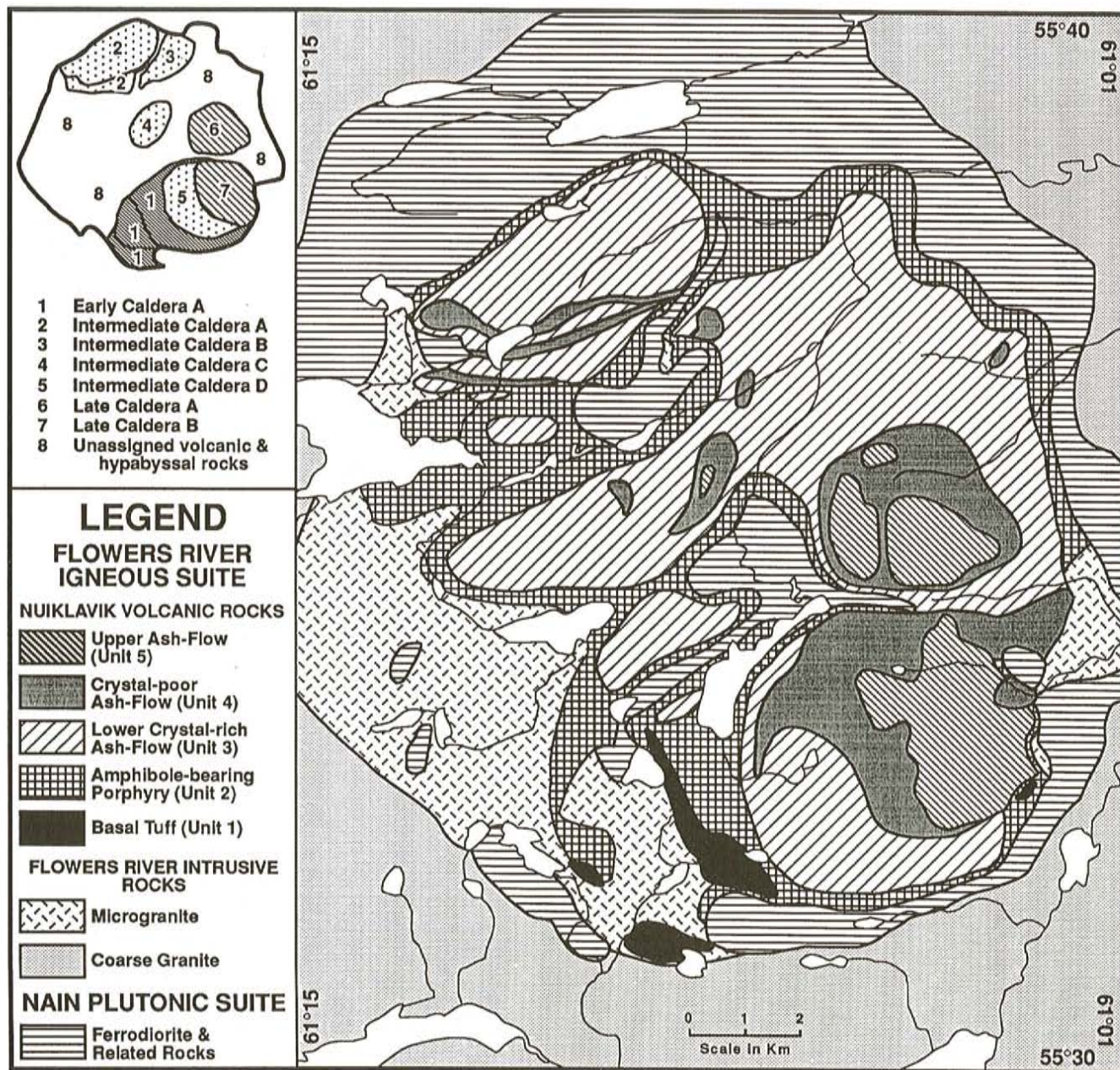
Rare-metal minerals are very small (with the exception of sparse zircon grains) and have not been identified. The observed zircon grains appear to be unaltered, however, it is not possible to petrographically evaluate other rare-metal minerals.

Similar extreme alteration has not been observed or reported in the associated hypabyssal ring dykes or the nearby subvolcanic granites of the Flowers River intrusive rocks.

## CHEMISTRY

A representative suite of 30 samples of extremely altered to unaltered volcanic rocks from the Nuiklavik volcanic rocks was chosen to study the chemistry of the alteration process; the major- and trace-element chemistry of 11 of these samples is listed in Table 2. The most striking observation from the data in Table 2 is the almost complete absence of Na<sub>2</sub>O in some samples (i.e., less than 0.1 percent). Samples having very little or no Na<sub>2</sub>O are most often characterized by





**Figure 3.** *Geology of Flowers River cauldron complex (R.R. Miller and A.M. Abdel-Rahman, unpublished data). Insert—recognized caldera structures in the cauldron complex.*

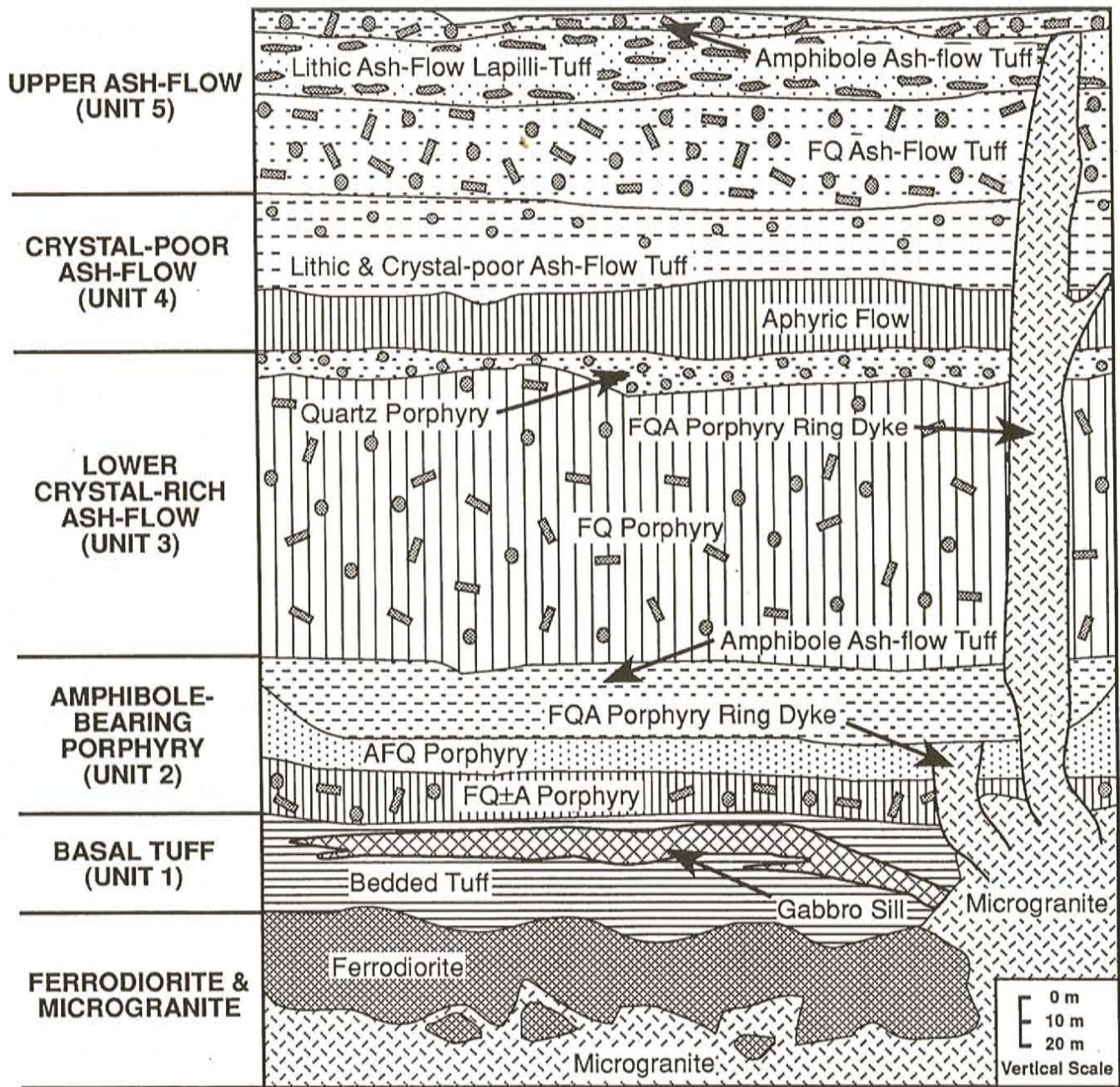
replacement of feldspar phenocrysts and groundmass feldspar by the green chlorite-like mineral (compare Table 1 and Table 2).

The extent of the Na-depletion is best observed in a  $\text{Na}_2\text{O}$ –Harker diagram (Figure 6) of the dataset, where  $\text{Na}_2\text{O}$  falls from almost 4 wt. percent to virtually 0 wt. percent; this diagram also indicates that Na-depletion is generally, but not always, accompanied by  $\text{SiO}_2$  enrichment. Figure 7 illustrates other geochemical trends that correlate with Na-depletion. These include a decrease in  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  and increases in  $\text{H}_2\text{O}$  and  $\text{ZrO}_2$ ;  $\text{H}_2\text{O}+$  provides the best

correlation with  $\text{Na}_2\text{O}$ . Generally, if a rock has any one of the following geochemical features then it will also have little or no  $\text{Na}_2\text{O}$  (Figures 6 and 7):  $\text{H}_2\text{O} > 1.0$  percent,  $\text{Al}_2\text{O}_3 < 10.5$  percent,  $\text{K}_2\text{O} < 3.8$  percent,  $\text{SiO}_2 > 77.5$  percent and  $\text{Zr} > 5000$  ppm; the opposite does not hold (e.g., rocks with  $> 3.8$  percent  $\text{K}_2\text{O}$  may also have little or no  $\text{Na}_2\text{O}$ ).

Some of the observations of the behaviour of various elements in low- $\text{Na}_2\text{O}$  rocks can be further tested by plotting some of these elements against each other (Figures 6 and 8). In these diagrams, the following is observed: 1)  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{H}_2\text{O}+$  and  $\text{K}_2\text{O}$  provide internally consistent plots, with





**Figure 4.** Generalized stratigraphic section of the Flowers River cauldron complex (R.R. Miller and A.M. Abdel-Rahman, unpublished data).

regard to  $\text{Na}_2\text{O}$  depletion, 2) overlap between the fields of Na-depleted and Na-enriched fields is observed in all plots with perhaps  $\text{H}_2\text{O}$  vs  $\text{Al}_2\text{O}_3$  providing the best separation between fields, 3)  $\text{K}_2\text{O}$  vs  $\text{SiO}_2$  gives the best approximation of a linear plot and 4)  $\text{ZrO}_2$  and  $\text{SiO}_2$  are not internally consistent (see Discussion). The scatter in these plots and the overlap between fields of Na-poor and Na-rich rocks are characteristic of an alteration process affecting various precursor rocks to varying degrees.

The rare-metal mineralization in the cauldron complex can best be characterized by plotting rare-metals against each

other (Figure 9; Zr vs Y, Zr vs Nb). These plots, in contrast to the plots of most major elements, illustrate highly correlated straight-line relationships between most pairs of rare-metals and other incompatible elements (e.g., REE, Y, Nb, Zr, U, Th). The plot of  $\text{ZrO}_2$  vs  $\text{SiO}_2$  (Figure 6) illustrates the chaotic relationship observed between incompatible elements and major elements in the cauldron complex; total Fe as FeO (Figure 9) is the only major element that exhibits a relatively good correlation with incompatible elements. Some compatible trace elements (Sc and Ba) also exhibit good correlation (i.e., negative correlation) with the incompatible elements (Figure 9; Zr vs Ba).



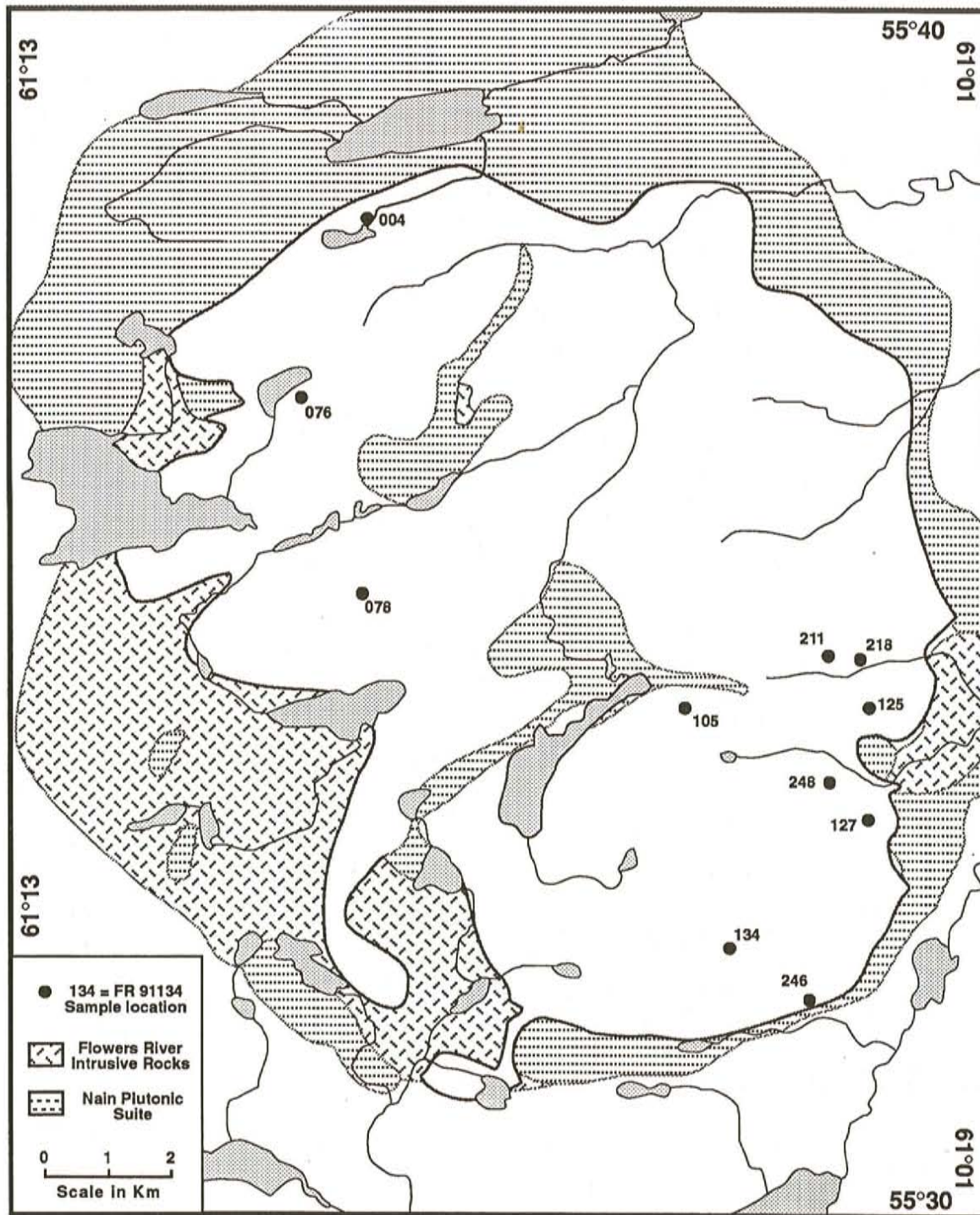


Figure 5. Sample locations in the Flowers River cauldron complex.

Some of the relationships between trace elements, rare-metal mineralization and the  $\text{Na}_2\text{O}$  depletion process can be illustrated in normalized diagrams (Figure 10). Hill and Thomas (1983) demonstrated that rocks in the Flowers River cauldron complex have trace-element affinities with comendites and pantellerites in unaltered volcanic suites. A relatively unaltered comendite obsidian, from the Naivasha complex, Kenya Rift Valley, was used as a normalizing factor

for this study (MacDonald *et al.*, 1987, Table 4, sample no. 301a). Thus, values near one on the normalized diagrams indicate chemical compositions near those of this comendite and values much higher or much lower than one indicate higher or lower chemical compositions. Figure 10 is arranged in a matrix with the left-hand column for high Na rocks ( $> 1.2$  percent  $\text{Na}_2\text{O}$ ) and right-hand column for low Na rocks ( $< 0.2$  percent  $\text{Na}_2\text{O}$ ); the rows represent rows of equal Zr,



**Table 1.** Characteristics of alteration in study samples\*

Sample	Unit No.	Rock Type	Feldspar	Matrix	Mafic Minerals
FR91004	3	Feldspar-quartz ash-flow	minor sericite & chlorite	chlorite	chlorite
FR91076	4	Aphyric ash-flow	—	?	chlorite
FR91078	3	Quartz ash-flow	30% replaced by chlorite	chlorite	—
FR91105	4	Aphyric ash-flow	—	chlorite	chlorite
FR91125	4	Altered feldspar-quartz ash-flow	sericitized	chlorite	chlorite?
FR91127	5	Feldspar-quartz porphyry (ring dyke ?)	relatively unaltered	unaltered	amphibole
FR91134	4	Quartz-poor ash-flow	—	chlorite	—
FR91211	4	Quartz-feldspar ash-flow breccia	sericite & hematized chlorite	chlorite	—
FR91218	3	Quartz ash-flow (zeolites)	—	—	—
FR91246	3	Quartz-feldspar ash-flow	sericite & hematized chlorite	chlorite	—
FR91248	4	Aphyric ash-flow	—	minor chlorite	—

\* Thin section observations

with Zr increasing downward. The similar patterns for high-Na and low-Na rocks at equal Zr values (i.e., compare two diagrams in any row) readily illustrates that most trace elements are relatively unaffected by the Na-depletion event. The columns of the matrix also illustrate the pattern of increasing U, Th, REE, Nb, Y, Be, Zn and Rb with increasing Zr and decreasing Ba and Sc with increasing Zr.

## DISCUSSION

### NATURE OF THE ALTERATION PROCESS

Certain features of the alteration process are readily apparent and clearly distinguished from magma differentiation and other processes. The mineralogical features of the alteration process indicate that, 1) Na was lost from albitic feldspar upon replacement by chlorite; 2) H<sub>2</sub>O was added to both phases in micropertthite to form chlorite and sericite; and 3) Fe was added to albite to make chlorite. It is less clear whether K, Al, Fe or Si are mobile or immobile during the alteration event. These mineralogical-petrographical features can only indicate what is happening to a particular mineral and do not tell us whether chemical components are mobile or conserved on the outcrop or hand-sample scale.

The geochemical data confirm that Na was lost from the system during the alteration process. Correlation of low Na from obviously highly altered rocks with other elements gives an indication that high H<sub>2</sub>O and Si and low K and Al may also result from the alteration process. Data from other studies suggests that K is unaffected by the process (Hill, 1982) and that depletion of Si and Na and enrichment of Al and Fe accompany the chloritization process (White, 1980). Some of these conclusions are contradictory if mineral-scale processes are compared to hand-sample scale processes but may be resolvable on the hand-sample scale (i.e., other minerals may be forming or may be replaced elsewhere in the system to conserve one or more of the elements giving the contradictory conclusions). Hand-sample scale data (i.e.,

whole-rock chemical data) indicate that rocks containing high H<sub>2</sub>O and Si and low K and Al are more likely to be altered. The FeO<sup>total</sup> vs Na<sub>2</sub>O data plot clearly indicates that FeO<sup>total</sup> does not correlate with Na<sub>2</sub>O, thus, FeO<sup>total</sup> is conserved on an outcrop scale and Fe used by chlorite to replace albite is obtained from within the host rock.

Studies of more recent peralkaline volcanic rocks (e.g., Mayor Island—Weaver *et al.*, 1990; Kenya Rift Valley—Baker and Henage, 1977) indicate that crystallization and devitrification of obsidians and other glassy rocks can lead to quantifiable loss of Na and other elements but the amount of Na-depletion is commonly less than 20 percent of the original Na. The addition of H<sub>2</sub>O to feldspar to form sericite and chlorite and the correlation of high H<sub>2</sub>O with low Na<sub>2</sub>O indicate that the replacement process is due mainly to hydrothermal activity; devitrification or crystallization may be responsible for a small component of the Na depletion.

### RELATIONSHIP BETWEEN THE ALTERATION AND DIFFERENTIATION PROCESSES

The volcanic rocks in the FRCC are either the products of one large magma chamber or a series of small magma chambers fed from a common source (R.R. Miller and A.M. Abdel-Rahman, unpublished data). As such, individual volcanic units are samples of the magma chamber(s) as it evolved and thus, should exhibit some kind of chemical differentiation trend. The Na-depletion process, a post-deposition process, imprints its chemical signature on top of that produced by magma differentiation. Trends observed on data plots used to characterize the Na-depletion process must be evaluated to determine what effect the underlying differentiation trend has.

It is commonly observed that differentiation of peralkaline magmas leads to declining Al<sub>2</sub>O<sub>3</sub>, as observed in Figure 6, and increasing SiO<sub>2</sub>, although not to the extremes in Figure 6. Thus, the correlation of low Al<sub>2</sub>O<sub>3</sub> with low Na<sub>2</sub>O may be completely or partially due to the differentiation



A



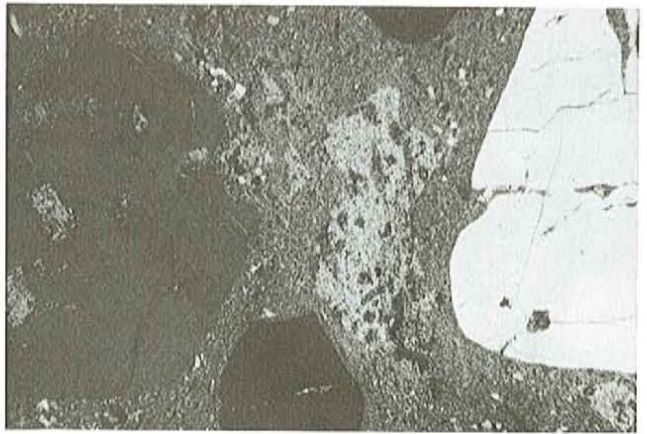
B



C



D



E



F



**Plate 1.** Photomicrographs of feldspar and mafic mineral alteration in peralkaline ash-flow tuffs. a) Photomicrograph: unaltered feldspar in a feldspar-quartz porphyritic ash-flow tuff; resorbed quartz and sub-euhedral feldspar; x-nicols, 2.5 x power (FR92091). b) Photomicrograph: incipient chloritic alteration of feldspar in a feldspar-quartz ash-flow tuff; chlorite in matrix and chlorite patches in feldspar; 2.5 x power (FR91291). c) Photomicrograph: extreme chloritic alteration of feldspar in a feldspar-quartz ash-flow tuff; 2.5 x power (FR91034). d) Photomicrograph: extreme sericitic alteration of feldspar in a feldspar-quartz ash-flow tuff; subhedral to resorbed quartz surrounding feldspar phenocryst replaced by light-coloured sericite; x-nicols, 2.5 x power (FR91125). e) Photomicrograph: chloritic alteration of feldspar in the groundmass of an aphyric ash-flow tuff; groundmass consists of chlorite and quartz; 2.5 x power (FR91105). f) Photomicrograph: alteration of alkali-amphibole to chlorite; elongate and equant amphibole phenocrysts completely replaced by chlorite; 2.5 x power (FR91033).



**Table 2.** Geochemical data for poorly to extremely altered Nuuklavik volcanic rocks<sup>^</sup>

Sample Unit #	1004 <sup>o</sup> 3	1076 4	1078 3	1105 4	1125 4	1127 5	1134 4	1211 4	1218 3	1246 3	1248 4
SiO <sub>2</sub>	75.05	75.65	80.80	79.40	76.65	73.60	75.10	77.55	86.30	75.85	72.85
TiO <sub>2</sub>	0.31	0.23	0.26	0.38	0.30	0.29	0.40	0.25	0.26	0.26	0.25
Al <sub>2</sub> O <sub>3</sub>	11.61	9.85	10.45	10.46	10.85	10.63	8.70	8.91	10.14	10.88	10.66
Fe <sub>2</sub> O <sub>3</sub>	1.21	1.15	0.89	0.96	0.97	2.55	1.63	6.62	0.70	2.63	3.31
FeO	1.77	5.05	1.35	2.04	5.06	2.71	5.57			1.71	3.15
FeO <sup>tot</sup> *	2.86	6.09	2.15	2.90	5.93	5.01	7.04	5.96	0.63	4.08	6.13
MnO	0.06	0.08	0.01	0.03	0.07	0.06	0.10	0.04	0.01	0.04	0.06
MgO	0.26	0.02	0.10	0.03	0.04	0.02	0.03	0.10	0.01	0.15	0.06
CaO	0.47	0.16	0.01	0.01	0.01	0.14	0.01	0.04	0.06	0.03	0.15
Na <sub>2</sub> O	3.60	0.05	0.01	0.05	0.05	3.70	0.01	0.08	0.11	1.21	3.06
K <sub>2</sub> O	4.51	4.43	3.11	2.88	3.10	4.56	2.06	3.46	0.63	4.86	4.29
P <sub>2</sub> O <sub>5</sub>	0.03	0.01	0.04	0.03	0.01	0.01	0.02	0.01	0.02	0.01	0.01
H <sub>2</sub> O+	0.48	1.65	1.97	1.86	2.08	0.50	2.47	1.60	1.56	1.96	0.95
H <sub>2</sub> O-	0.21	0.22	0.27	0.28	0.20	0.13	0.24	0.17	0.32	0.35	0.17
S	0.02	0.07	0.00	0.03	0.01	0.04	0.02	0.02	0.05	0.02	0.14
CO <sub>2</sub>	0.19	0.09	0.11	0.07	0.06	0.12	0.27	0.06	0.04	0.10	0.13
Total*	99.89	99.41	99.48	98.73	99.86	99.41	98.19	100.00	100.31	100.25	99.91
A.I.	0.93	0.50	0.32	0.31	0.32	1.04	0.26	0.44	0.09	0.67	0.91
Rb	161	542	181	145	257	277	295	721	33	218	389
Ba	252	23	61	91	21	37	29	31	45	84	20
Sr	28	9	3	3	3	7	4	11	8	9	12
Pb	233	169	39	25	43	65	134	228	<1	18	68
Zn	285	516	34	54	165	312	606	506	15	106	454
La	174	359	119	245	250	278	766	534	58	158	364
Ce	367	1006	273	473	647	688	2237	1542	139	329	689
Y	92	499	71	137	264	249	1161	792	50	131	525
Th	13	82	9	9	46	35	247	164	18	18	92
Sc	1.7	<0.1	1.2	0.7	0.1	0.2	<0.1	<0.1	1.4	0.3	<0.1
U	3.3	14.2	2.5	2.9	8.8	6.2	42.4	23.7	7.5	3.1	12.4
Zr	808	5185	743	1595	2935	2585	11569	8094	747	1443	4937
Nb	57	350	48	74	180	164	766	521	45	95	365
F	338	1200	214	250	380	747	447	622	221	98	397

<sup>^</sup> Extremely altered samples have Na<sub>2</sub>O < 0.10 percent

<sup>o</sup> Add FR9 to this number to obtain sample number

• FeO<sup>tot</sup> = total Fe calculated as FeO

\* Total includes ZrO<sub>2</sub>

– Trace elements in ppm; ICP and AA analysis, Newfoundland Geological Survey Branch Laboratory;

– U by neutron activation; F by specific ion electrode;

– Major elements in wt. %; ICP analysis, Newfoundland Geological Survey Branch Laboratory;

– CO<sub>2</sub>, S and H<sub>2</sub>O+ by IR analysis.

– A.I. = Agpaite Index = molar ((Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>)

process. Felsic volcanic rocks with over 76 percent SiO<sub>2</sub> are commonly considered to be non-representative of magma compositions (i.e., silicified rocks or rocks with cumulate quartz). In the FRCC, high SiO<sub>2</sub> rocks (> 78 percent SiO<sub>2</sub>) contain low values of Na<sub>2</sub>O suggesting that the high SiO<sub>2</sub> may be due to the Na-depletion event or perhaps a separate silicification event.

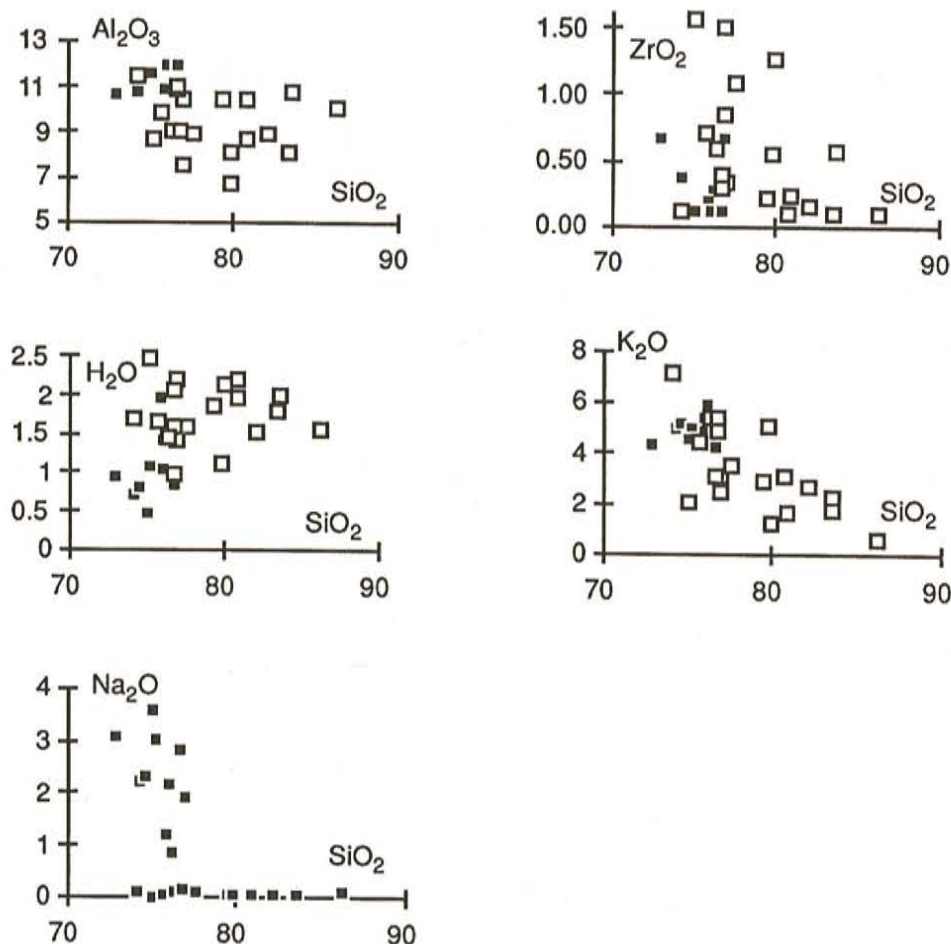
The decline of K<sub>2</sub>O in Figure 6 is contrary to normal

peralkaline differentiation trends, suggesting that the occurrence of low K<sub>2</sub>O in low Na<sub>2</sub>O rocks is probably connected to the Na-depletion process.

#### RELATIONSHIP BETWEEN THE ALTERATION AND MINERALIZATION PROCESSES

Rare-metal mineralization in peralkaline granites and volcanic rocks is thought to be due to either a metasomatic





**Figure 6.** Harker diagrams of altered and relatively unaltered rocks ( $\text{Na}_2\text{O}$ ,  $\text{ZrO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ); filled squares are relatively unaltered samples (all samples in  $\text{Na}_2\text{O}$  vs  $\text{SiO}_2$  plot); unfilled squares are altered samples ( $\text{Na}_2\text{O} < 0.2$  wt. percent).

(i.e., hydrothermal) event (e.g., Salvi and Williams-Jones, 1990a,b; Ramsden *et al.*, 1993) or the formation of incompatible enriched residual liquids in a magma chamber (e.g., Birkett and Miller, 1990). If the rare-metal mineralization (Zr, Y, Nb, REE) in the FRCC is due to a metasomatic event then it is most likely related to the Na-depletion hydrothermal event.

The  $\text{ZrO}_2$  vs  $\text{SiO}_2$ , the  $\text{SiO}_2$  vs  $\text{Na}_2\text{O}$  and the Zr vs  $\text{Na}_2\text{O}$  plots (Figures 6 and 7) clearly indicate that either  $\text{ZrO}_2$  or  $\text{SiO}_2$  are not involved in the Na-depletion event. High  $\text{SiO}_2$  values ( $> 80$  percent  $\text{SiO}_2$ ) correlate with low  $\text{ZrO}_2$  ( $< 0.6$  percent  $\text{ZrO}_2$ ), whereas it has been established that high  $\text{SiO}_2$  and high  $\text{ZrO}_2$  correlate with low  $\text{Na}_2\text{O}$ . Several lines of evidence suggest that Zr and the other incompatible elements are relatively immobile during the Na-depletion process: 1) the excellent correlation of Zr vs the other incompatible elements (Figure 9) contrasts significantly with the scatter plots of  $\text{SiO}_2$  vs other major elements (Figure 6) and  $\text{SiO}_2$  vs the incompatible elements (Figure 6); 2) Ba and Sc exhibit excellent correlation with incompatible elements (Figure 9), whereas  $\text{SiO}_2$  vs Ba or Sc plots are scatter plots; 3) comparison of selected trace-element normalized plots for  $\text{Na}_2\text{O}$ -rich ( $> 1.2$  percent) vs  $\text{Na}_2\text{O}$ -poor ( $< 0.2$  percent) at

comparable Zr values (Figure 10) gives identical plots for rare-metals, Zn, Ba and Sc, 4) the lack of petrographic evidence of the growth of rare-metal-bearing minerals in conjunction with chloritization of feldspar, and 5) the lack of correlation of rare-metals with  $\text{Na}_2\text{O}$  (Figure 7).

The high positive correlation of Zr, Y, Nb, U, Th, and REE and the high negative correlation of rare-metals with Ba and Sc (Figure 9) strongly argue for a magmatic process for the concentration of rare metals in the Nuuklavik volcanic rocks.

This conclusion does not account for the fact that all high-Zr samples ( $> 5000$  ppm) contain little or no  $\text{Na}_2\text{O}$  ( $< 0.1$  percent), contrary to all known peralkaline differentiation trends. However, all known occurrences of volcanic rocks with  $> 5000$  ppm Zr occur in Unit 4, which generally appears to be the upper limit of Na-depleted rocks. This observation indicates that at least some and perhaps all of the hydrothermal activity responsible for Na depletion and feldspar replacement is related to Unit 4 volcanism. If Unit 4 volcanism was accompanied by high levels of hydrothermal activity, then Unit 4 volcanic rocks were probably most susceptible to the Na-depletion process.



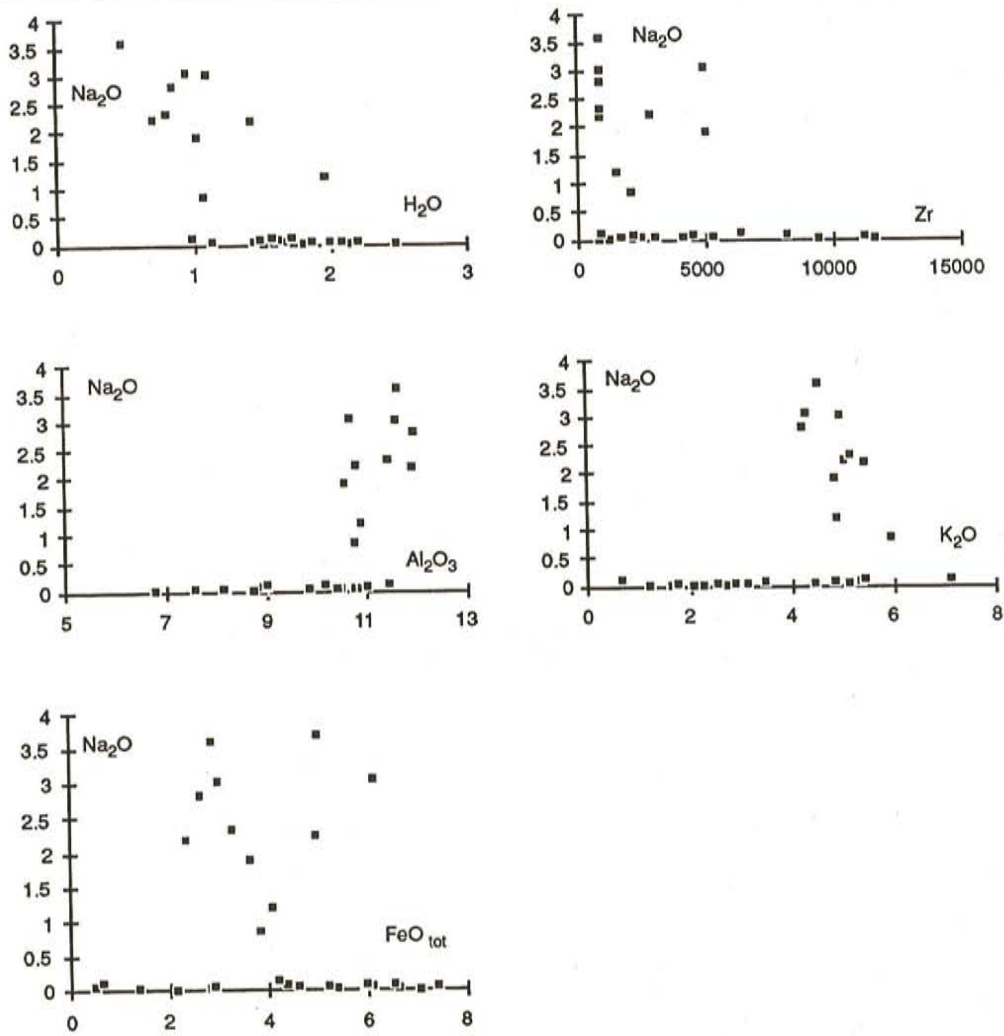


Figure 7. The relationship between the Na-depletion process and other elements;  $\text{Na}_2\text{O}$  vs  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , Zr,  $\text{H}_2\text{O}$ ,  $\text{FeO}^{\text{tot}}$ .

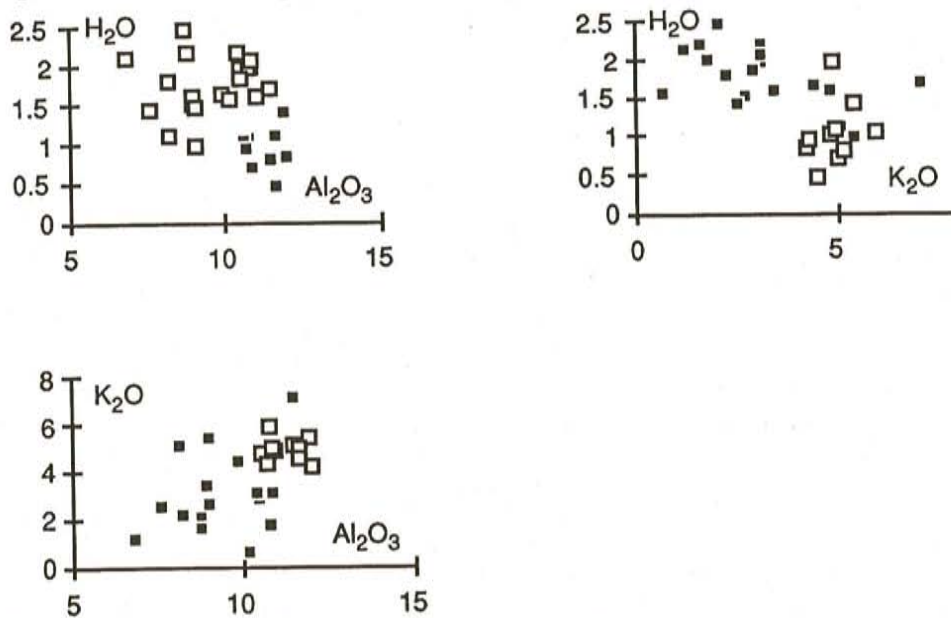


Figure 8. The relationship between elements potentially involved in the Na-depletion process ( $\text{H}_2\text{O}$  vs  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}$  vs  $\text{K}_2\text{O}$ ,  $\text{K}_2\text{O}$  vs  $\text{Al}_2\text{O}_3$ ); filled squares are relatively unaltered samples ( $\text{Na}_2\text{O} > 1.2$  wt. percent); unfilled squares are altered samples ( $\text{Na}_2\text{O} < 0.2$  wt. percent).



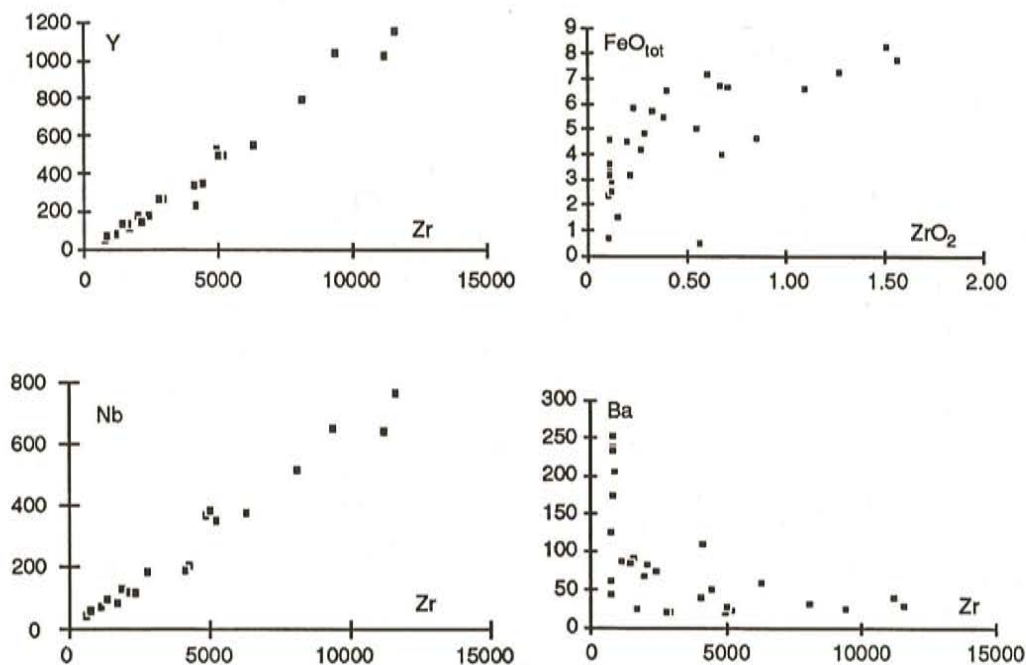


Figure 9. The relationship between incompatible elements (Zr vs Y, Zr vs Nb), compatible and incompatible elements (Zr vs Ba) and  $FeO^{total}$  vs  $ZrO_2$ .

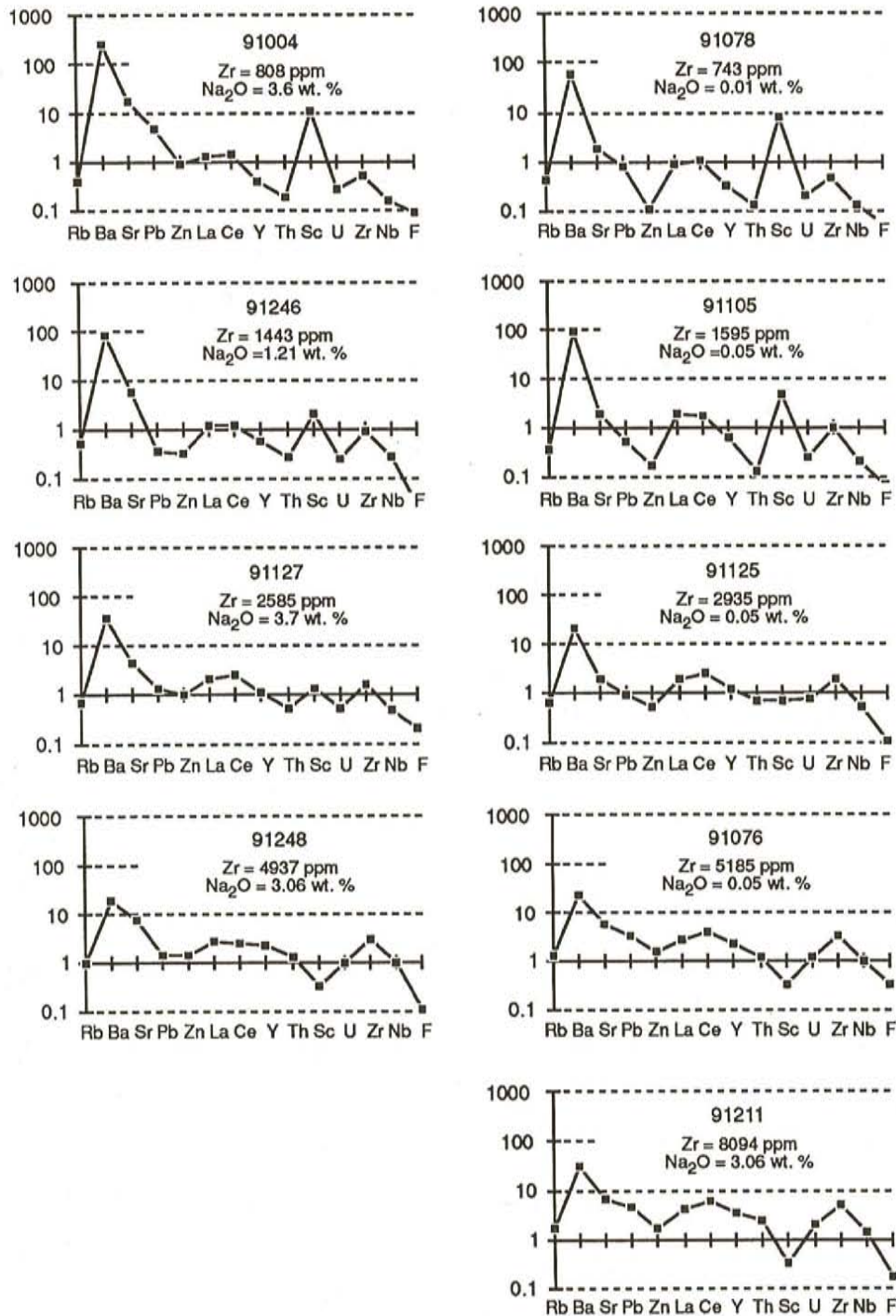
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**Figure 10.** Comendite normalized trace-element data for a suite of Na-poor and relatively Na-rich rocks of various Zr concentrations. The normalizing data is from sample 30la (MacDonald et al., 1987), a comenditic obsidian from the Naivasha complex, Kenya Rift Valley. High Na samples are found in the left-hand column and low Na samples in the right-hand column. Rows contain samples of nearly equivalent Zr concentrations. Compare samples in any row to determine the effect of the Na-depletion event on trace elements on rocks of similar Zr concentrations. Elements are in order of relative ionic radii.



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*Note: Geological Survey Branch file numbers are included in square brackets.*